Competition between Charge Ordering and Superconductivity in Layered Organic Conductors α-(BEDT-TTF)$_2$$M$Hg(SCN)$_4$ (M = K, NH$_4$)

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While the optical properties of the superconducting salt α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ remain metallic down to 2 K, in the non-superconducting K-analog a pseudogap develops at frequencies of about 200 cm^{-1} for temperatures $T < 200$ K. Based on exact diagonalisation calculations on an extended Hubbard model at quarter-filling we argue that fluctuations associated with short range charge ordering are responsible for the observed low-frequency feature. The different ground states, including superconductivity, are a consequence of the proximity of these compounds to a quantum phase charge-ordering transition driven by the intermolecular Coulomb repulsion.

Electronic and magnetic systems in low dimensions display a number of exciting phenomena which have been the subject of many experimental and theoretical investigations [1]. Ideal realizations of such systems are the organic conductors in which the effect of strong electronic correlations in the ground state properties is under intense investigation [2]. For example, in the one-dimensional Bechgaard salts TMTSF and TMTTF, superconductivity, charge ordering, and spin-density-wave instabilities are observed below a metallic state (which is described by a Fermi-liquid or a Luttinger liquid, depending on the strength of the interchain coupling) [2,3]. Significant progress has been achieved in understanding their properties in comparison to the quasi two-dimensional materials, for which the theoretical models and experimental studies are much less advanced. While some members of the BEDT-TTF family (where BEDT-TTF or ET stands for bisethylenedithio-tetrathiafulvalene), which serves as a model system for layered conductors, become superconducting, others remain metallic down to the lowest temperatures accessible, and others undergo metal-to-insulator transitions [4]. This is in contrast with band structure calculations which predict a metallic state for most of these salts.

Besides the well-studied κ-phase compounds, the α-phase family of (BEDT-TTF)$_2$$M$Hg(SCN)$_4$ has attracted considerable attention after superconductivity at $T_c = 1$ K was found in the NH$_4$-salt [5]. In contrast, the M= K, Rb, and Tl-salts, remain metallic down to a few mK entering a density-wave ground state at $T_p \approx 8$ K to 12 K which is highly controversial [6–8]. It was suggested that a low-temperature reconstruction of the Fermi surface induced by a Peierls distortion [9] occurs in $M =$ K, Rb, and Tl-salts but not in the NH$_4$-compound. However, the Fermi surfaces calculated for all of these compounds are almost identical, consisting of two-dimensional closed pockets [10] and quasi-one-dimensional open sheets. This topology was confirmed by a number of quantum-oscillation studies [11]. Hence, the different ground states encountered are difficult to understand from band structure calculations. In the present Letter, we introduce a scenario based on comprehensive optical investigations combined with exact diagonalisation calculations, in which electronic correlations play an essential role. We show that the proximity of these materials to a quantum phase transition driven by the intermolecular Coulomb repulsion can explain the different ground states found in the various salts.

Optics has proven to be a powerful method to explore the ground state of low-dimensional metals [12]. In K$_{0.3}$-MoO$_3$ or TTF-TCNQ, for example, clear signatures of a charge density wave have been observed in the optical spectra, like the opening of a single particle gap in the infrared and collective excitation in radio-frequency and microwave range [13]. Similar fingerprints (but at lower energies) of a spin-density-wave ground state have been identified in (TMTSF)$_2$PF$_6$ [12]. Recently the development of a pseudogap in the two-dimensional metal (BEDT-TTF)$_4$[Ni(dto)$_2$] was related to the strong Coulomb interaction, and we predicted that it should also play an important role in the α-type compounds [14].

Single crystals of α-(BEDT-TTF)$_2$KHg(SCN)$_4$ and α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ (denoted by K-salt and NH$_4$-salt) of about $1.5 \times 1 \times 0.3$ mm^3 in size were studied by polarized optical reflection methods in the frequency range from 50 to 10 000 cm^{-1} at 4 K $< T <$ 300 K. Figs. 1a and c show the reflectivity spectra $R(\omega)$ of both compounds obtained for the electric field $E \parallel a$ (a corresponds to the stacking direction) at different temperatures. In Ref. [15,16] we have analyzed the vibrational features of both salts in detail. Common to many organic conductors, the room-temperature reflectivity decreases

gradually for increasing frequency with no pronounced plasma edge [17]. Going down to low temperatures, an overall rise in reflectivity is observed in the NH_4-salt, but no drastic changes of the general behavior; this is expected for a metal. While at frequencies above approximately 500 cm^{-1} the temperature dependences of both compounds are similar, in the K-salt a new feature is observed at lower energies: a significant dip in the reflection centered around 200 cm^{-1} gradually develops as T drops below 200 K (Fig. 1a). Perpendicular to the a-axis the reflectivity of both materials exhibits a plasma edge around 5000 cm^{-1} which becomes more pronounced with decreasing T (insets of Fig.1). Again, no significant changes are observed with lowering T for the NH_4-salt; the K-compound, however, exhibits a dip in the reflectivity around 200 cm^{-1} for $T \leq 200$ K which is identical to the other polarization.

For the Kramers-Kronig analysis [12] we used a Hagen-Rubens extrapolation for $\omega \rightarrow 0$; above 7000 cm^{-1} we utilized the standard optical behavior known from other BEDT-TTF compounds and finally extrapolated by $R \propto \omega^{-4}$. The corresponding conductivity $\sigma(\omega)$ is plotted in the lower frames of Fig. 1. The two compounds exhibit a similar room temperature behavior, only the absolute values of the NH_4-salt are slightly higher. For both polarizations their conductivity shows a Drude-like peak and a broad maximum near 2000 cm^{-1}. The shift of the spectral weight to lower energies as T decreases agrees with the dc resistivity [18]. In the mid-infrared range the absolute values of both directions differ by a factor of 2. At $T = 300$ K the overall shape, however, is not so much different for the two polarizations in spite of the anisotropic Fermi surface; only when the temperature is lowered these differences become stronger. The dip in $R(\omega)$ observed in the K-salt in both polarizations shows up as a maximum in the conductivity spectra slightly above 200 cm^{-1} due to excitations across the pseudogap. The position of the peak is the same for both orientations and does not change with temperature; the spectral weight increases linearly by about a factor of 5 when going from $T = 200$ K to 4 K [18]; no signs of a phase transition around $T_p \approx 8$ K are observed in our spectra. In agreement with previous studies [15] we do not find indications of a pseudogap in the NH_4-compound.

In Fig. 2 the low-temperature conductivity of the two materials is compared for both polarizations. The strong feature is clearly seen in the spectra of the K-salt at around 200 cm^{-1} where $\sigma(\omega)$ drops by 50%. A narrow Drude-like contribution with a scattering rate of less than 30 cm^{-1} remains which contains only a few percent of the spectral weight; nevertheless it is responsible for the dc conductivity and the quantum oscillations [11]. The overall scenarios are similar in both directions.

In the last decade a large number of investigations have been performed on the low-temperature phase of α-$(BEDT-TTF)_2KHg(SCN)_4$. The transition at $T_p \approx 8$ K

is associated with a change in the Fermi surface [19,20] which could open a charge gap along the a-direction; of course large parts of the Fermi surface remain intact leading to the metallic dc conductivity and quantum oscillations. A small modulation of the magnetic moments suggest a spin-density-wave ground state [21,22]; but also a charge-density-wave instability was recently suggested [7,8,23]. The magnetic field dependence of the transition temperature is controversial [6,24]. Above a so-called kink-field $B_k \approx 24$ T the metallic state is restored [6] but maybe a new phase emerges [23,25]. The interpretation of the measured optical spectra of α-type BEDT-TTF salts in terms of a charge-density-wave instability, faces several difficulties: (i) the strong T dependence of the 200 cm^{-1} feature between 4 K and 200 K, is incompatible with semiconductor-like excitations. (ii) The negligibly small anisotropy in the optical response seems inconsistent with the large anisotropy of the crystal structure, (iii) The dip in the reflectivity of the K-salt can be observed up to $T \approx 200$ K, which is difficult to associate with the low-temperature density-wave ground state. In order to overcome the above difficulties, we find it necessary to consider both the *intramolecular* Coulomb repulsion U, as well as the *intermolecular* Coulomb interaction V. Indeed, we show that the V-term is responsible for the subtle competition between the different ground states appearing in α-$(BEDT-TTF)_2MHg(SCN)_4$.

It is known that Coulomb interaction leads to unconventional behavior of the electronic properties of layered organic materials [4,17]. For instance, the optical conductivity of κ-type compounds display a Drude peak at low temperatures which is suppressed for $T > 50$ K, in contrast to conventional metals [26]. This is in agreement with dynamical mean-field-theory calculations [27] on a frustrated lattice at half-filling with strong on-site Coulomb repulsion $U \approx W$ (W being the bandwidth). Since in κ-salts the BEDT-TTF molecules are dimerised, the conduction band is half-filled. The quasiparticles are destroyed with increasing T because the system is close to a Mott metal-insulator transition. This is not the case in the α-salts as they are quarter-filled with holes. For instance, Hartree-Fock calculations in a Hubbard model with $U = 0.7$ eV suggest a paramagnetic metallic ground state for the K-compound [28]. Including the nearest-neighbor interaction V, however, can lead to charge-ordering phenomena [29]. Recent exact-diagonalisation calculations on an extended Hubbard model at quarter-filling [30] show that a transition from a metal to a checkerboard charge ordered insulator occurs at $V = V_c^{MI} = 2.2t$, where t is the nearest-neighbors hopping. Also there is a strong redistribution of the spectral weight in the optical conductivity. Calculations of the optical conductivity on a 4×4 square lattice are shown in Fig. 3 for $U = 20t$ and different values of $V < V_c^{MI}$. We find a broad resonance and a sharp peak located at frequencies of about 2t. When the

system is insulating, the calculated spectra consists of a single broad resonance centered at $\omega \approx 3V$; this is the energy cost for moving an electron inside the checkerboard. However, for small values of V the checkerboard is not fully formed, the energy cost being smaller than $3V$. We associate this broad resonance resulting from the calculations shown in Fig. 3 with the 2000 cm^{-1} band experimentally observed. On the other hand, we attribute the low frequency feature to the enhancement of charge fluctuations associated with short range charge ordering. We note that as V/t increases this resonance shifts down slightly and the intensities of both the broad band and the sharp peak are enhanced. For $V \leq 0.5t$ the spectrum is dominated by the Drude peak, in agreement with the optical conductivity observed for the NH$_4$-salt. Note that the strong enhancement of the sharp feature occurs already at $V \approx t$. Our calculations are in qualitative good agreement with the evolution of the measured optical spectra when going from the NH$_4$-salt to the K-analog if we assume that V/t increases from the former to the latter. We note that the Fermi surface considered in the calculations does not have any special property (for the quarter-filled square it consists of a featureless closed sheet only), making our results robust against changes in its shape.

In order to explain why superconductivity occurs in the NH$_4$-salt but not in the corresponding K-compound, we consider results from many-body calculations on an extended Hubbard model at quarter filling. Slave-boson theory predicts the appearance of superconductivity mediated by charge fluctuations which are present on the metallic side of the phase diagram close to the charge-ordering transition [32]. This suggests that superconductivity in NH$_4$ is a consequence of its proximity to a charge-ordering instability driven by the ratio V/t. Hence, α-(BEDT-TTF)$_2$KHg(SCN)$_4$, which is at the charge-ordered side of the transition, *i.e.* $(V/t)_{\mathrm{K}} > (V/t)_{\mathrm{NH}_4}$, may be converted into a superconductor by decreasing V/t. Some attempts in this direction have already been carried out by applying external pressure [6]. Uniaxial strain provides a better way to tune the materials through the transition because decreasing a/b (where a is the intra-stack and b the inter-stack distances) favors a metallic state. As a matter of fact, T_c increases from 1.5 K up to about 6 K in the NH$_4$-compound; and most important, superconductivity is also reached for the K-salt when sufficient pressure is applied along the a-direction [33]. The above scenario is consistent with superconductivity at quantum phase transitions observed in numerous systems [4]. Hence the NH$_4$-salt can be driven closer to the charge-ordering transition by increasing V/t; superconductivity should disappear, and eventually we expect a redistribution of the spectral weight due to the gradual enhancement of dynamically induced charge fluctuations. In contrast to the K-compound, for the superconducting NH$_4$-salt the Coulomb repulsion is not strong enough to induce charge ordering. Releasing the pressure sufficiently should suppress superconductivity and eventually lead to a charge-ordered insulator.

In conclusion, we have investigated the optical properties of the metallic ($M = $ K) and superconducting ($M = $ NH$_4$) compounds of α-(BEDT-TTF)$_2M$Hg(SCN)$_4$. Due to the closer proximity to a charge-ordering quantum phase transition, the K-salt shows a strong feature in the electronic spectrum at about 200 cm^{-1} while the optical conductivity of the NH$_4$-compound remains metallic at all temperatures until the system eventually becomes superconducting. From exact diagonalisation calculations we identify the low-frequency feature with the gradual enhancement of fluctuations associated with short range ordering close to a charge-ordering transition. This scenario may be tested by applying uniaxial strain to tune the materials through the transition and induce superconductivity in the K-salt. Further experiments using X-ray and Raman scattering are necessary to provide additional evidence of charge ordering phenomena in the α-salts.

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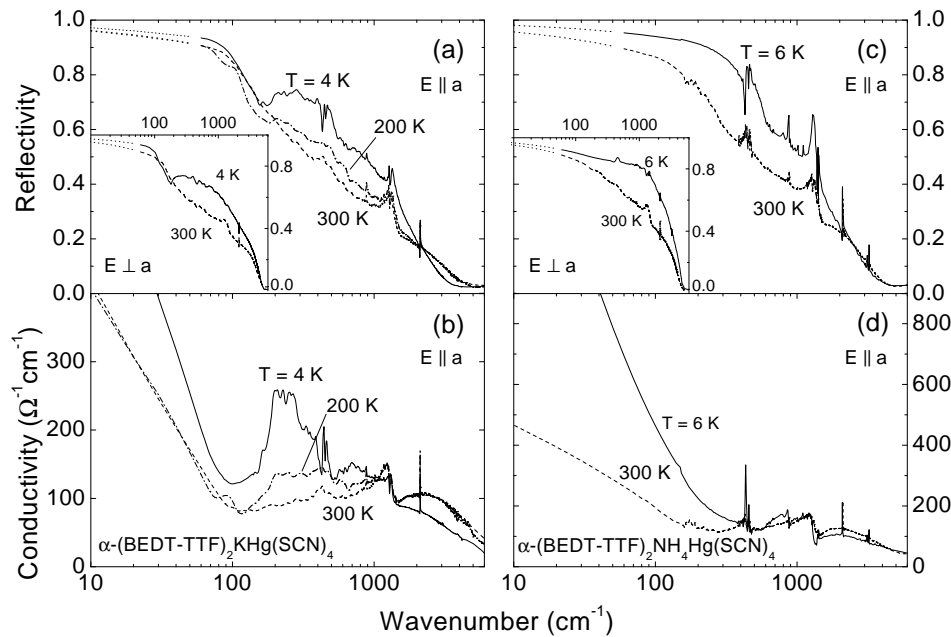FIG. 1. (a) Frequency dependent reflectivity and (b) optical conductivity of α-(BEDT-TTF)$_2$KHg(SCN)$_4$ for different temperatures as indicated. The panels (c) and (d) show the reflectivity and conductivity, respectively, of α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$. The measurements were performed for $E \parallel a$; the $E \perp a$ reflection data are displayed in the corresponding insets. For both polarization the reflectivity of (BEDT-TTF)$_2$KHg(SCN)$_4$ has a dip at around 200 cm^{-1}.
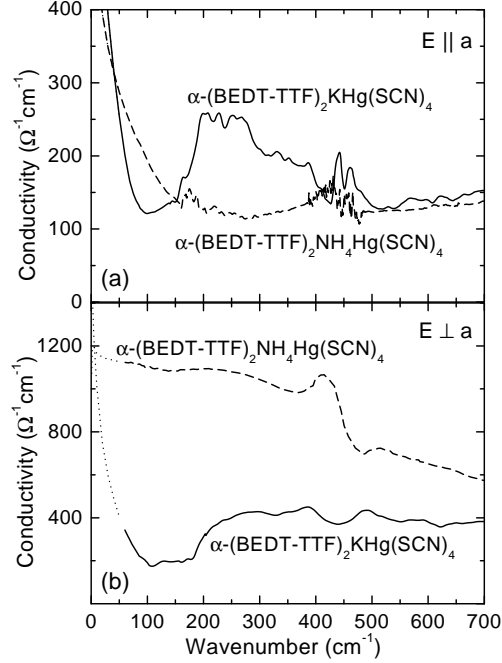
FIG. 2. Optical conductivity of α-(BEDT-TTF)$_2$KHg-(SCN)$_4$ (solid lines) and α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ (dashed lines) obtained at $T = 4$ K for the electric field polarized (a) parallel and (b) perpendicular to the a-axis. In both directions of (BEDT-TTF)$_2$KHg(SCN)$_4$ a pseudogap feature is clearly seen at 200 cm^{-1} which is not present in the superconductor (BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$.
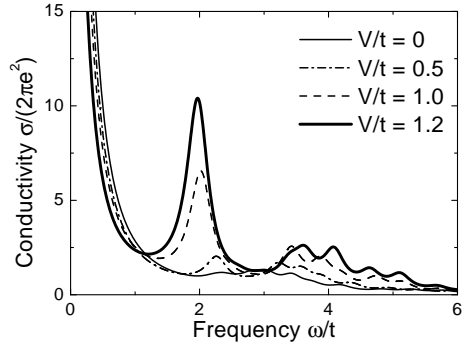

FIG. 3. Evolution of optical conductivity as the system is brought closer to the charge ordering transition. The optical conductivity obtained using exact diagonalisation of an extended Hubbard model on a 4×4 square lattice with fixed $U = 20t$ is plotted for increasing intersite Coulomb repulsion V. A strong feature develops at low frequencies associated with fluctuations due to short range charge ordering. Note that for these values of V the system is well in the metallic side of the transition: $V < V_c^{\mathrm{MI}} \approx 2.2t$.